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Construction of nuclear magnetic resonance spectroscope and its calibration

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CONSTRUCTION OF NUCLEAR MAGNETIC RESONANCE
SPECTROSCOPE AND ITS CALIBRATION

A Thesis

Presented to

The Faculty of the Department of Chemistry
University of the Pacific

In Partial Fulfillment
of the Requirement for the Degree of
Master of Science

by

Irshad Ahmad

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Introduction

The concept of nuclear spin and magnetic moment was developed at about the same time as the analogous properties of the electron. It was first suggested by Pauli (11) in 1924 that the hyperfine structure observed in atomic spectra could be explained if it were assumed that the nuclei of certain isotopes were associated with a magnetic moment. Dennison (6) in 1927 showed from heat capacity studies that ordinary Hydrogen consists of two molecular species (Ortho and Para Hydrogen), which differ in the symmetry of their nuclear spin wave functions. Thus by 1930 the concept of nuclear spin and magnetic moment was well accepted.

Stern and Esterman (7), for the first time, determined the magnetic moment of the proton by the atomic beam deflection method. However, Rabi (15) and associates, in 1939, used another technique. They deflected the atomic or molecular beam in an inhomogeneous magnetic field and then irradiated it with a radio wave, the magnetic vector of which causes the beam to retrace the deflection. From the various components known, the magnetic moment of the nuclei was calculated.

The Nuclear Magnetic Resonance Spectroscopy as used today involves the same principles as embodied in the Rabi's method, described above; the difference between

the two techniques is of experimental nature only. The phenomenon of nuclear magnetic resonance was first observed by Edward Purcell (14) and associates at Harvard and Felix Bloch (2) and associates at Stanford, independently in 1946. Again the difference between the methods was of experimental technique. In the Purcell method a single coil was used around the sample which was connected to the signal generator as well as to the receiver through a R.F. bridge. The adjustment for the resonance to be observed was made through the bridge. In the Bloch method, also called the two coil method, two different coils with their axes at right angles were used around the sample. The receiver coil picked up the signals because of the magnetic induction by the Transmitter coil. In this method the resonance was observed as a dip in the curve on the Oscilloscope screen.

The importance of N.M.R. Spectroscopy to Chemistry was not realised till Arnold, Dharamati, and Packard (1) reported the spectra of methyl and ethyl alcohol in 1951. They found that methyl alcohol absorbed at two different frequencies; whereas ethyl alcohol absorbed at three different frequencies. This was a little strange because the only nucleus absorbing the frequency was Hydrogen and till that time there was no method available to distinguish between the same nucleus in different molecular environments. The three frequencies in the Spectrum of ethyl alcohol were attributed to the $-OH$, $-CH_2$, and $-CH_3$ groups.

Arnold et al also suggested that the method, because it differentiates between Hydrogen atoms with different electronic distributions could be used for the investigation of chemical structure, reaction rates and chemical equilibria. Soon after, Gutowsky and Hoffman (8) studied the spectra of PF_5^{19} and IF_5^{19} and found that these compounds gave two different peaks. The appearance of two resonance lines in the spectrum of these compounds indicates non-equivalent electronic distribution in the structurally distinguishable bonds. Soon after the importance of N.M.R. Spectroscopy was established more sophisticated instruments (10) started coming into use. At present High Resolution Spectroscopes which are of the self-recording type are extensively used in research.

However, the high cost of the instrument prevents its use in smaller and poorer schools. In recent years a low cost instrument of the single coil type has been constructed by the Aero Medical Laboratory (16) which is alright for demonstration purposes but cannot be used for research because of low resolution. The idea of the present project was to see whether a similar instrument of double coil type could be made at a low cost of about \$200. This instrument could give the proton resonance peak of water and be used for demonstration purposes. However, it cannot be expected that such an instrument could be used in research. Because of non-availability of funds and lack of a well equipped electronic workshop, self-made electronic

components or Heath-Kit type instruments have been used. As a permanent magnet was available, a constant field type spectroscope has been preferred for construction.

Theory

The nuclei of certain isotopes possess an intrinsic mechanical spin, that is, they are associated with definite angular momentum. According to the general principles (12) of quantum mechanics, the maximum measurable component of angular momentum of a nucleus must be equal to an integral or half integral multiple of the value of $h/2\pi$, where h is the Planck constant. If we write the maximum component as $Ih/2\pi$, then I is called the Spin quantum number. Also a nucleus with spin I will have $(2I + 1)$ orientations in space. In absence of a magnetic field all these states will have identical energy.

As the nucleus is charged, the spin of the nucleus will produce a magnetic momentum. If the distribution of the charge is spherical (for $I = 1/2$) the nucleus will have a dipole moment; but if the distribution of the charge is non-symmetrical (for $I > 1$ or $= 1$) the nucleus will also have a quadrupole moment. For simplicity, let us consider a proton which behaves as a magnetic dipole. When the proton is placed in a magnetic field, the proton has $2I + 1$ i.e. two orientations. These two states will be characterised by different energies; one of them will have higher potential energy than the other. If the dipole moment of the proton be denoted by μ , then these two states will have energies $-\mu H$ and $+\mu H$. Because of the different

energy levels of the proton a transition is possible. On calculation it is found that for a magnetic field of the order of one to ten kilogauss the radiation frequency will be in the Radio frequency range. Generalizing the above property of the proton, we can show that any nucleus with spin I will have $(2I + 1)$ possible orientations which will be characterized by different Potential energies when placed in a magnetic field. According to the Selection Rule the transition can occur only to the next energy level, i.e. with the difference of the two spin quantum numbers being 1. By calculation it is found that the energy difference between any two successive levels will be $\mu H/I$. The radio frequency to cause the transition between the two levels must satisfy the Bohr frequency condition.

$$h\nu = \frac{\mu H}{I} \quad 1)$$

Since the magnetic moment and the angular momentum behave as parallel vectors, they must be proportional; the proportionality constant is called the Magneto-gyric ratio. Thus

$$\mu = \gamma \left\{ I \cdot \frac{h}{2\pi} \right\} \quad 2)$$

Combining equations 1) and 2) we get

$$\nu = \frac{\gamma H}{2\pi}$$

3)

which is the basic frequency-field relationship for the nuclear magnetic induction.

When a nucleus is placed in a magnetic field, the dipole is acted upon by a torque. If it were a static dipole the effect would be just a deflection of the magnetic axis. But the nucleus is spinning; hence the effect will be an altering of the axis of rotation continuously so that each pole of the axis sweeps out a circular path. This imposed motion is called Precession and it can be shown that the precessional frequency will also be given by equation 3). Now when a nucleus is in a fixed field the precession frequency is also fixed. If we use a signal generator and vary the frequency there will be no change observed till the radio frequency equals the Precessional frequency. This stage is called as Resonance because the electromagnetic field and the axis of the rotation of the nucleus are oscillating at the same frequency. The resonance frequency has the right amount of energy to cause the transition from one energy level of the nucleus to the next. Thus at this stage the nucleus will absorb energy from the Radio frequency. This is called Nuclear Magnetic Resonance. The condition of resonance can also be reached by keeping the radio frequency constant and varying the

magnetic field.

If we superimpose on a constant field (in Z direction) an oscillating magnetic field in X direction² the paramagnetic polarization originally parallel to the field will be forced to precess about the field with a latitude which decreases as the frequency of the oscillating field approaches the Larmor frequency. For frequencies near the Resonance frequency an oscillating induced voltage can be expected in a pick up coil placed with its axis parallel to the Y direction. Simple calculation shows that with reasonable apparatus dimensions the signal power from the pick up coil will be substantially larger than the thermal noise power in a practicable frequency band.

Thus a nucleus with a certain magnetic moment (i.e. with spin I greater than zero) will show absorption at a certain frequency in a fixed field. As the magnetogyric ratios of different isotopes are different, the absorption will occur at different frequencies. Besides the nucleus is surrounded by electrons; as a result the effect of the field on the nucleus depends on the electronic distribution around it. Thus the absorption frequency for the same nucleus in different molecular environment will be different. So the absorption frequency of a proton in methyl group will be different from that in hydroxyl group, because the electronic distribution around the proton in the two cases are different. Because of this reason Nuclear Magnetic Resonance Spectroscopy can

distinguish between chemical bonds. A parameter, characteristic of this feature, called Chemical Shift (17) is very helpful for identifying certain nuclei in different chemical grouping. A chemical shift tells us how much the frequency of a nucleus in a certain group differs from that of the same nucleus in a standard compound. Mathematically it is defined as

$$\delta = \frac{\nu_s - \nu_r}{\nu_r}, \text{ when the field is fixed}$$

and
$$\delta = \frac{H_s - H_r}{H_r}, \text{ when the frequency is}$$

fixed. The subscript r refers to the reference compound and the subscript s refers to the sample under investigation. In general the standard substance chosen is the solvent itself, which is usually water. The chemical shift for various groups have been determined and are available in literature (9). They are usually expressed as parts per million. Thus

$$\delta = \frac{H_s - H_r}{H_r} \times 10^6$$

Thus by determining the chemical shift of various peaks of an unknown compound its structure can be elucidated. Also it has been found that the area under each peak is proportional to the number of the same contribu-

ting nuclei in that compound. In this way qualitative and quantitative analysis of compounds is possible with the help of Nuclear Magnetic Resonance Spectroscopy. Besides various magnetic properties of the compound and their interactions can also be studied.

In the Spectroscope the two requisites needed are sharper and higher peaks and higher resolution of the peaks. As for a particular nucleus the chemical shift is constant, it is evident that a high resolution spectroscope should employ a strong magnetic field. The sharpness of the peaks and their height is increased by rotating the sample. This was first done by F. Bloch, W. W. Hansen, and M. E. Packard (3). They also provided an explanation for this effect and that was that by spinning the sample the homogeneity of the field is increased. When the sample is spun with a particular speed, each molecule is exposed to the same average magnetic field, and hence the field over the entire sample is virtually constant.

The separation of the resonance (12) lines is measured either by the Side Band Technique or by the Wiggle Beat Method. The first one is simpler and the accuracy of the method is about one cycle or better. The principle of the method is that when an audio-frequency of low amplitude modulates the magnetic field, side bands appear on either side of the resonance signal. The audio frequency is varied till the side band on right side of one resonance line coincides with the side band on the left side of the

other resonance signal. At this stage the separation of the two resonance lines is equal to the audio-frequency. The wiggle beat method is more accurate and has an accuracy of ± 1 cycle per second. This method is based on the transient-decay phenomena of the resonance signal under rapid passage conditions. In the spectra the single resonance signal is followed by a series of exponential decaying oscillations called wiggles. When two or more closely spaced components of the resonance signal have constant separation of the wiggles of the individual signals will be out of phase and will give rise to wiggle beats. Also it can be shown by simple calculations that when the mutual separation of the component signals is J , in cycles second, the time between successive beat maxima is equal to $1/J$ seconds. Thus by measuring the time between two successive beat maxima, the separation of signals can be calculated. Also this method is independent of sweep speed and sweep linearity. The ratio of different types of nuclei can be determined either by measuring the area under each peak or by measuring the intensities of the signals. We plan to use the first method.

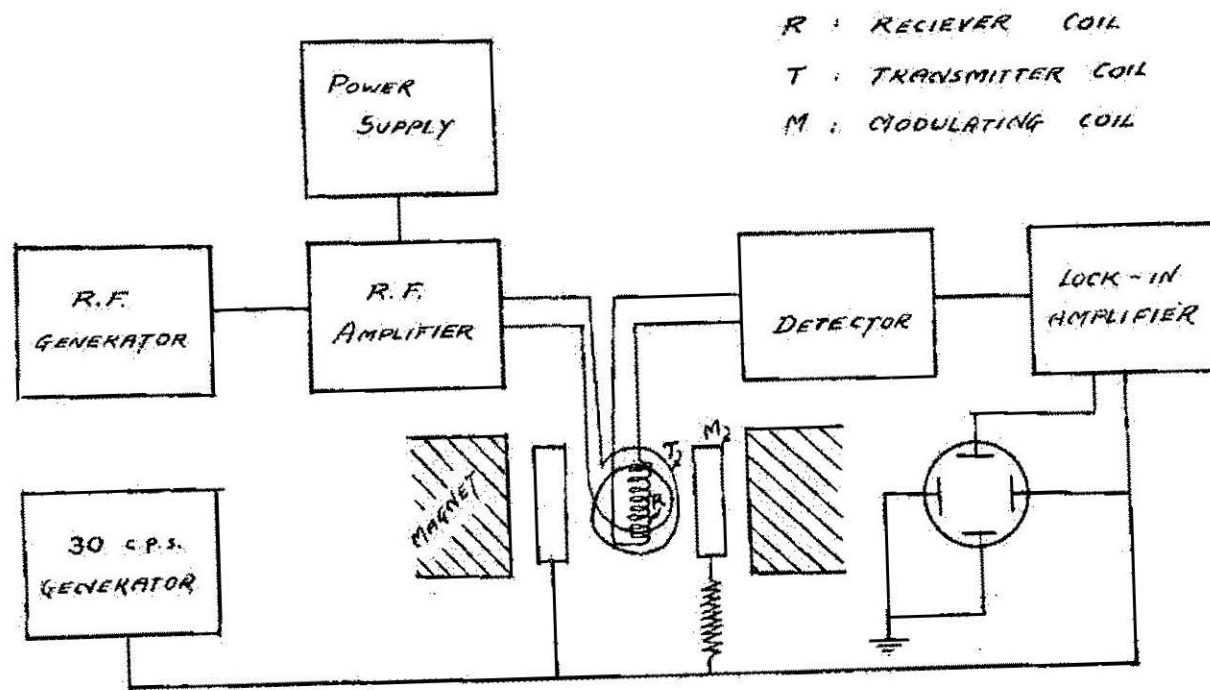


Figure 1
Block Diagram

Experimental Procedure

As mentioned earlier, a Bloch type NMR Spectroscope of constant field has been constructed. However, there is a little difference in the instrument, which is due to Proctor (13). Instead of a usual type of audio-amplifier a Lock-in type amplifier has been used. All components of the instrument have been built in this laboratory; some are built according to the circuits available in the literature and others are Heath Kit instruments assembled in this laboratory. The block diagram is given in Fig. 1 and the specifications of various components are discussed below.

The Permanent Magnet:

A uniform field magnet suitable for the NMR construction costs a few thousand dollars. But the magnet used in this instrument was taken out of a surplus magnetron. This magnet cannot satisfy the requirement of high uniformity of field needed for resonance. The pole pieces of the magnet are mounted on a soft iron base; one pole piece is fixed while the other is adjustable. The pole faces are rectangular and flat and are 3 x 5 inches in dimension. The gap between the pole pieces is 1 1/2 inches. The field strength as measured by the Fluxmeter is 3 kilogauss and can be varied by changing the gap between the pole pieces. The uniformity of the field could not be

checked because of lack of a good magnetometer.

The Signal Generator:

The General Radio 805 transmitter which is quite suitable for the construction of the spectroscope, is too costly for us to afford. Consequently a Heath Kit model IG-42 oscillator, assembled in this laboratory has been used. It covers a frequency range of 100 KC to 500 MC in 5 bands. The frequency range was calculated so that the resonance peaks of the most of the nuclei could be observed at a field strength of 3 kilogauss. The frequency of the oscillator was calibrated against a standard transmitter in the campus radio-television shop. The output of the transmitter was 0.1 volt which corresponds to a power of 0.1 milliwatt in the coil. The accuracy of the frequency is $\pm 3\%$.

The Radio Frequency Amplifier:

As the power required in the transmitter coil for the signal is about one watt, the present signal generator should be connected with an R.F. amplifier. The amplifier was designed and built in the television workshop. It is a three stage conventional amplifier and the circuit is shown in Fig. 2. It amplifies the signal by a factor of about two hundred. The signal power after the amplification is about 1.2 watt for the lower frequencies and about one watt for the higher frequencies, as measured by a voltmeter. The power to the amplifier was

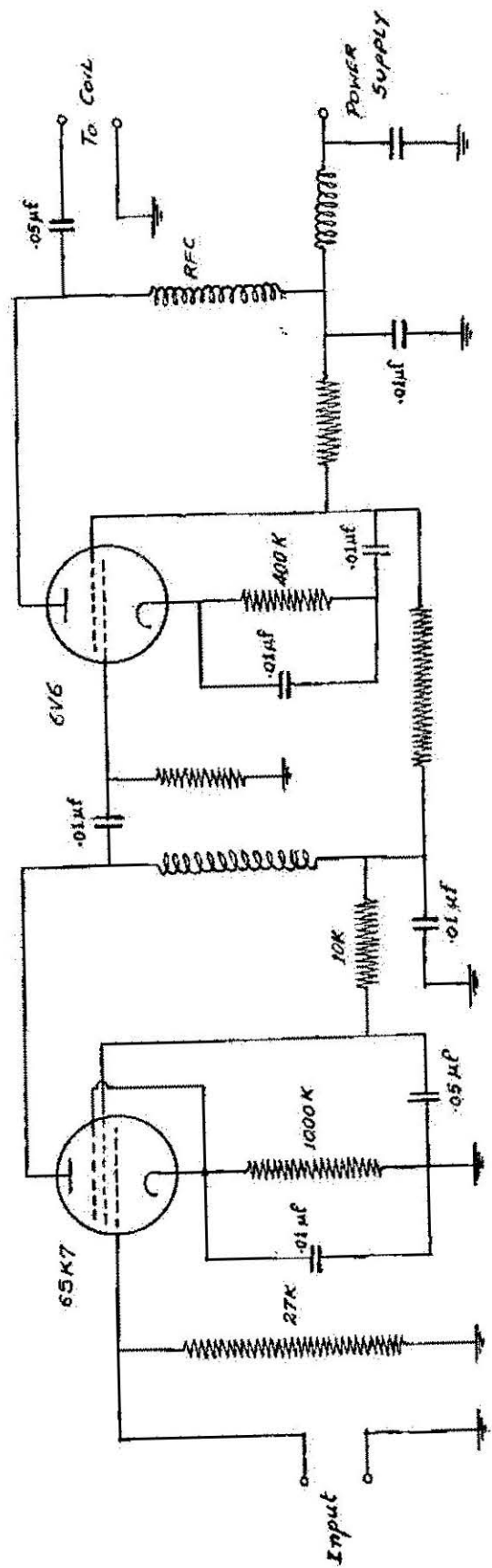


Figure 2
R.F. Amplifier

supplied by a Heath Kit model PS-3 Variable Voltage Regulated Power Supply which was also assembled in this laboratory.

The Probe Unit:

A polystyrene tube, $1/2$ inch in diameter and $3/4$ inch in length which is threaded inside contains 7 turns of thin enamelled wire and this acts as the transmitter coil. On another Polystyrene tube, $5/8$ inch in diameter and $3/8$ inch long which is threaded outside are wound 24 turns of thin enamelled wire and this acts as the receiver coil. It is, then slipped in the transmitter unit with its axis as accurately perpendicular to the axis of the transmitter coil as possible, and then fixed with Polystyrene cement. This whole unit is, then, placed in a small Aluminium box which has two projections on the side so that the whole unit may be placed in a proper fixed position between the pole pieces. The placing of the Receiver Coil within the Transmitter Coil is very important because, for the resonance to be observed, the angle between the two coils should be exactly $(5) \pi/2$. For good results the difference between this angle and $\pi/2$ should be of the order of 10^{-6} radians. The receiver coils is then connected to a tuning circuit, placed in an Aluminium box so that the receiver coil could be tuned to the resonance frequency. This will increase the pickup voltage at resonance.

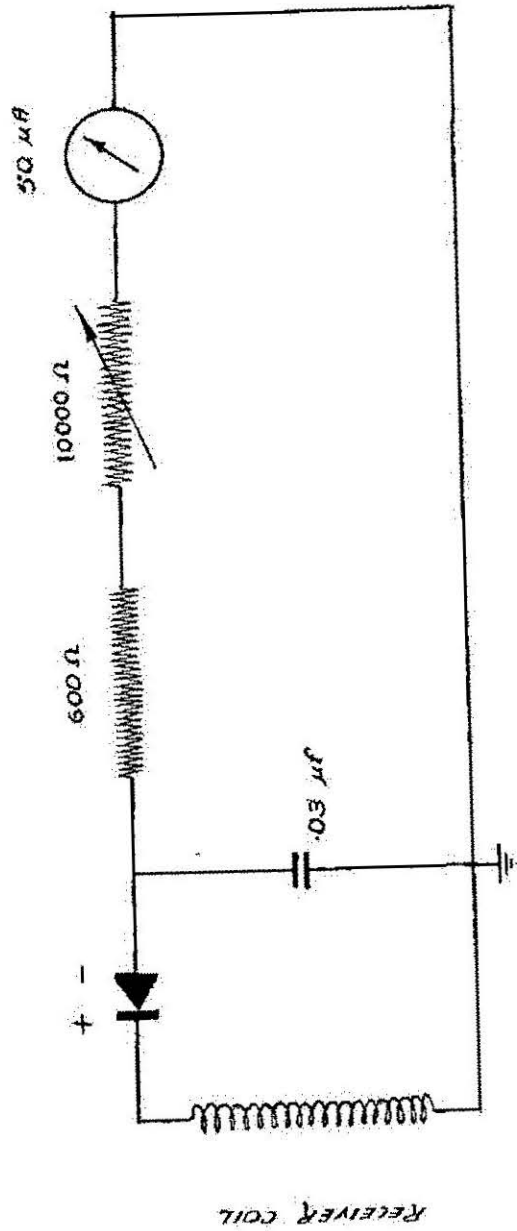


Figure 3
Detector

Detector:

A diode detector is used to detect the voltage picked up by the receiver coil. The Detector was built in the campus radio-television workshop and the circuit is shown in Fig. 3. The microammeter used in the circuit helps us get a rough measure of resonance beforehand. The output of the detector is fed to the Lock-in Amplifier.

Lock-in Amplifier:

In order to get a better resonance, a tuned phase-sensitive audio-amplifier (4) has been used. The circuit is shown in Fig. 4. The DC output of the detector is applied to the Lock-in Amplifier. The output is amplified, first by an ordinary amplifier stage which is then followed by a tuned amplifier stage, sharply tuned to the modulation frequency (in this case 30 cps.). The resulting signal is now mixed with a signal from the audio-oscillator in the two 6SJ7 tubes. The mixed signal is, then, detected by a 6SN7 tube, used as a difference amplifier. Thus we get the DC output which is applied to the vertical plates of the oscilloscope.

The twin-T feed-back filter stage tuned at 30 cps. is to reduce the influence of the harmonics and to prevent the overload of the later stages by spurious induction from power lines, etc.

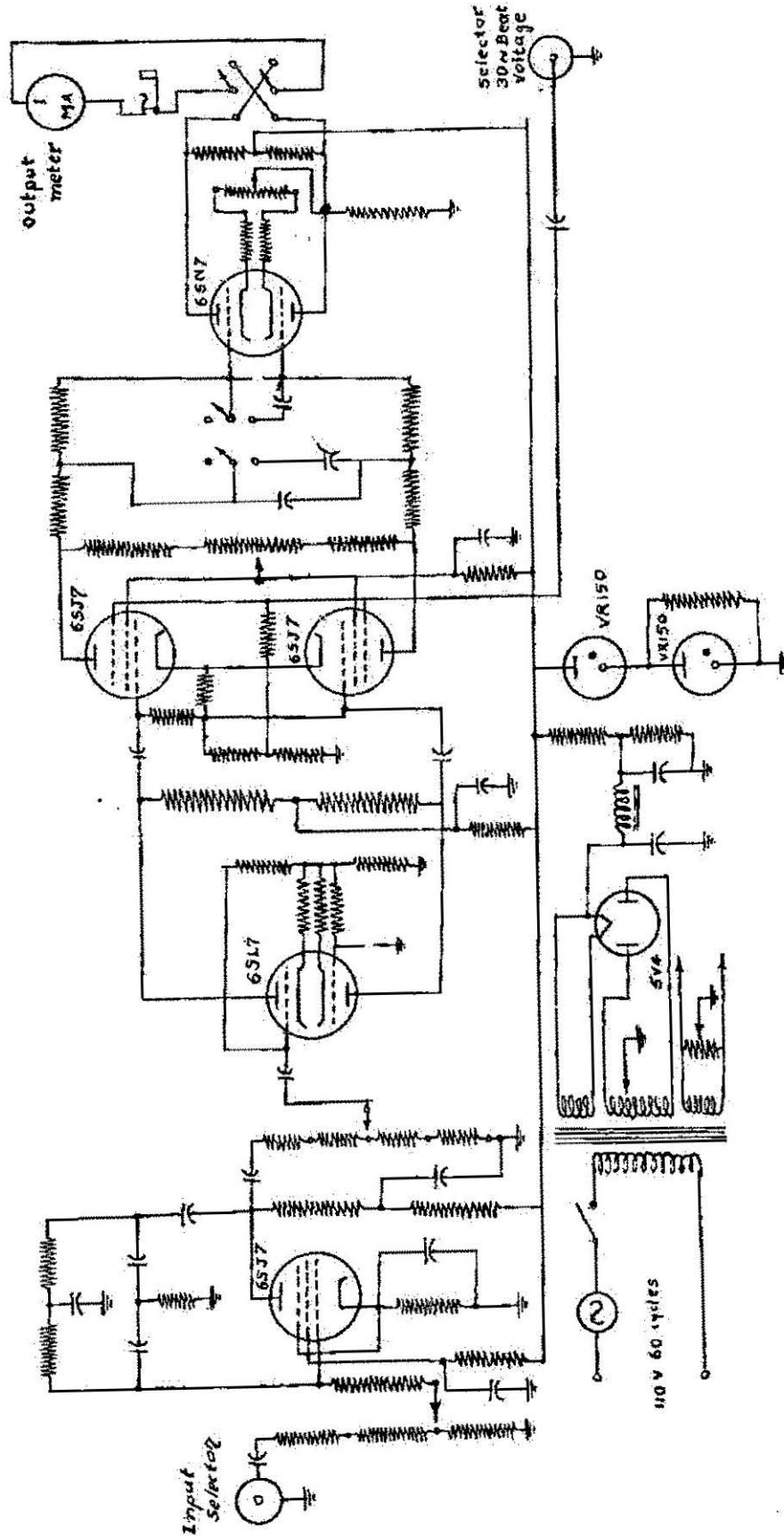


Figure 4
Lock-In Amplifier

Modulation Frequency Generator:

The modulation frequency of 30 cps. is applied to modulate the magnetic field between the pole pieces. It consists of a multivibrator to (4) trigger the frequency of the power lines viz 60 cps. to 30 cps., two RC tuned amplifier stages to filter out all other components except the 30 cps. one. It also contains a power amplifier which is a push-pull amplifier consisting of 6L6 tubes to provide the power for driving the modulating coils. It also contains a phase shift circuit and an amplification stage for the beat voltage on the suppressor grids of the audio-mixer, at the same time it serves as the horizontal sweep of the Oscilloscope. The use of 30 cps. excludes any response of the audio-amplifier to spurious 60 cps. signals or the harmonics thereof. Because the multivibrator was locked to the frequency of the power lines, possible zero drifts arising from slow changes in phase with respect to the mains were excluded.

The modulation coils consist of (4) 50 turns of enamelled copper wire around each pole piece. At 0.5 amp. current they could provide a 30 cps. sweep of about 3 gauss in amplitude (6 gauss in total). The modulating field could be varied up to 15 gauss maximum.

Oscilloscope:

The oscilloscope used in the instrument was a Heathkit model O-12 and was assembled in this laboratory. The maximum gain of the oscilloscope amplifier

was about 200.

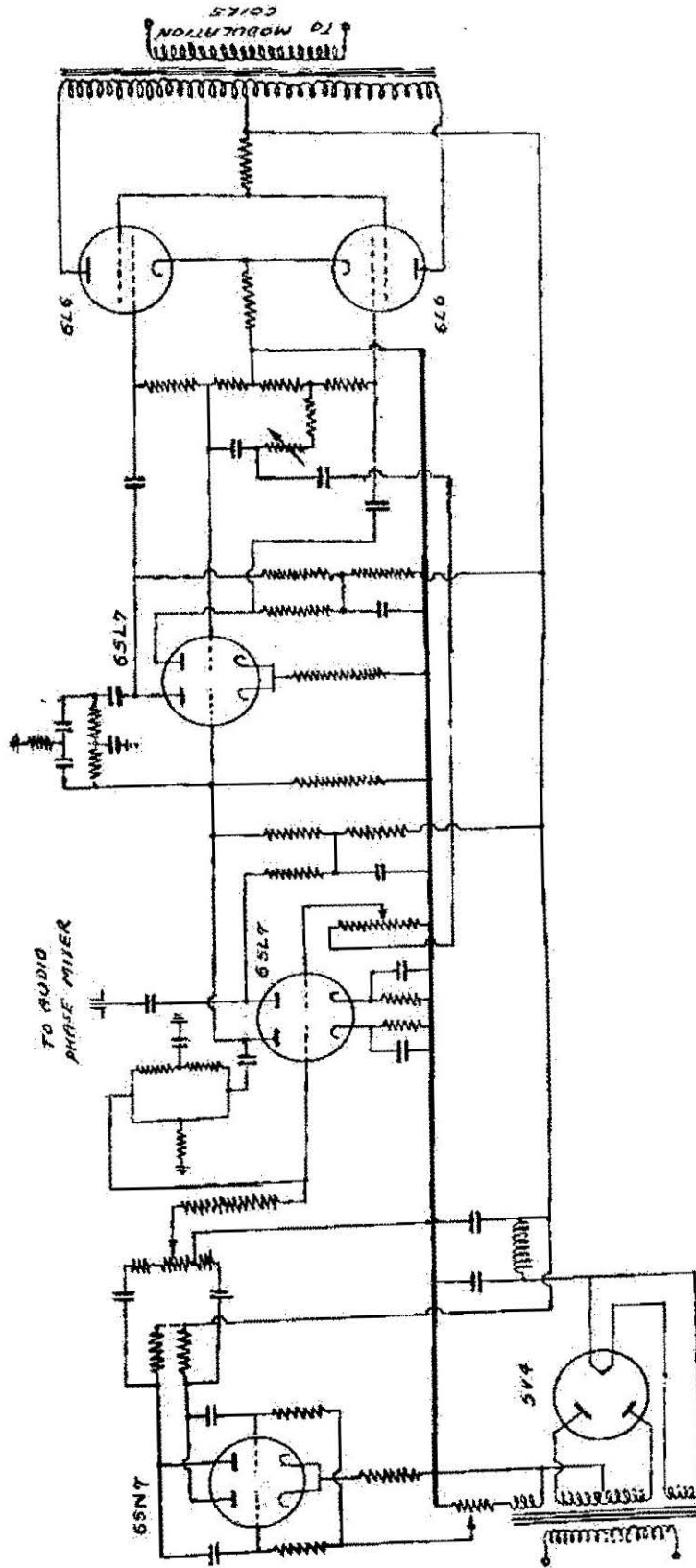


Figure 5

30 c.p.s. Generator

Testing

All parts of the instrument were turned on and were given about half an hour to warm up. The cell was made out of a glass tube, 5 mm in diameter and 2.5 cm. long. A solution of Ferric nitrate was used as the standard substance for the proton resonance. The solution of Ferric nitrate in water was placed in the cell and it was sealed. This was then placed in the probe unit so that it was inside the receiving coil. The magnetic field, as measured by the Gaussometer at a gap width of one inch was 2280 gauss. The frequency of radiation which would bring about the resonance at the above field was calculated to be 11.86 MC. Hence the frequency of the Oscillator was adjusted to that value. The sweep frequency was turned on also and the spectrum was observed on the oscilloscope screen and this was also indicated on the Micro-ammeter. No absorption peak was found at this frequency. By scanning it was found that a small peak occurs at 12 Mc. However, on further scanning downward it was found that a better absorption occurred at 8 Mc and also a small peak was observed at 4 Mc. Moreover, the absorption peaks were present even when the cell was taken out. This clearly showed that the absorption was not due to proton resonance. The absorption occurred because of resonance in the coils. Later on different coils were used in the probe unit but no proton resonance was observed.

Discussion and Conclusions

As mentioned in the previous paragraph, the instrument constructed by us could not give the water resonance peak. This simple experiment shows that an NMR Spectroscope built from components of ordinary quality does not have a high enough resolution so that the resonance peak could be observed. Hence to observe the peak one has to use very high quality components. With our limited budget we could neither afford these costly equipments, nor was it the purpose of the present project to use such high class equipment. As mentioned in the "Introduction" the idea was to see whether a low cost instrument of double coil type could be made to give the resonance peak of water. The failure of the instrument to give the water resonance peak is understandable because the condition for the resonance to occur is very stringent. In the first place the field has to be extremely homogenous (only a variation of few milligauss per gauss is tolerable), which is not satisfied by an average magnet like the one we used. Secondly the Radio frequency to cause the transition has to be very stable, otherwise the peak will be smeared and won't be seen on the oscilloscope. The third condition that the two coils have to be exactly at right angles to each other (within 10^{-6} radians) which is possible but hard to satisfy. Also the oscilloscope should have a very high gain and the other electronic components should be constructed such that

the system may have the minimum noise. As the ordinary components cannot satisfy these conditions, it is hard to observe the resonance peak with such type of instrument. However one purpose of the project is not lost that the instrument may still be used as a demonstration instrument. It will aid in the teaching and understanding of the construction and working of a Nuclear Magnetic Resonance Spectroscope.

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